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半枝莲的一个新的克罗烷二萜

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摘要: 从半枝莲 (*Scutellaria barbata*) 植物地上部分的甲醇提取物中分离得到一个新的克罗烷二萜。通过现代波谱技术鉴定为15β-甲氧基-6α-*O*-乙酰基-19-*O*-丙酰基-4α, 18; 11, 16; 15, 16-环氧-新克罗烷二萜。

关键词: 半枝莲; 唇形科; 克罗烷二萜
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Scutellin A, a New Neoclerodane Diterpenoid from *Scutellaria barbata* (Labiatae)

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Abstract: A new neoclerodane diterpenoid was isolated from the ethyl acetate extract of *Scutellaria barbata*. The structure was determined as 15β-methoxy-6α-acetoxy-19-propanoyloxy-4α, 18; 11, 16; 15, 16-triepoxy-neoclerodan.

Key words: *Scutellaria barbata*; Labiatae; Neoclerodane diterpenoid

The dried whole herb of *Scutellaria barbata* D. Don (named in Chinese as "Ban Zhi Lian") has been used in folk medicine for the treatment of tumors, heptitis, liver cirrhosis and other diseases in China (Kan, 1978). In previous researches, there were several reports about cytotoxic neoclerodane diterpenoids isolated from this species (Dai *et al.*, 2006; Dai *et al.*, 2007). The isolation of the methanol extraction of the aerial part of *Scutellaria barbata* led to obtain a new neoclerodane diterpenoid, Scutellin A (1). The structure was elucidated by 1D, 2D NMR and HRESIMS data.

Results and Discussion

Scutellin A (1) was isolated as white solid. Its molecular formula was deduced to be $C_{26}H_{40}O_8$ on the basis of NMR data and the positive HRESIMS at *m z* 503.2622 $[M+Na]^+$. Intensive absorption bands at 1725 cm^{-1} observed in IR spectra indicate the presence of carbonyl groups. ^{1}H and ^{13}C NMR spectra of Scutellin A exhibited characteristic signals of 4α, 18; 11, 16; 15, 16-triepoxy neoclerodane diterpenoid [δ_H 0.94 (s, H-20), 0.84 (d, *J* = 6.4, H-17), δ 2.97 (dd, *J* = 3.6, 2.4, Ha-18) 2.18 (d, *J* = 3.6, Hb-18), 3.99 (dd, *J* = 12.4, H-11), 5.08 (d, *J* = 4.8, H-15), 5.69 (d, *J* = 5.4, H-16), δ_C 13.9 (q, C-20), 17.4 (q, C-17), 48.3 (t, C-18), 83.5 (d, C-11), 104.8 (d, C-15), 107.2 (d, C-16)] (Lin *et al.*, 1989; Ohno *et al.*, 1996). The ^{1}H and ^{13}C NMR data also gave signals of one methylene [δ_H 4.39 (d, *J* = 12.0, Ha-19), 4.83 (d, *J* =

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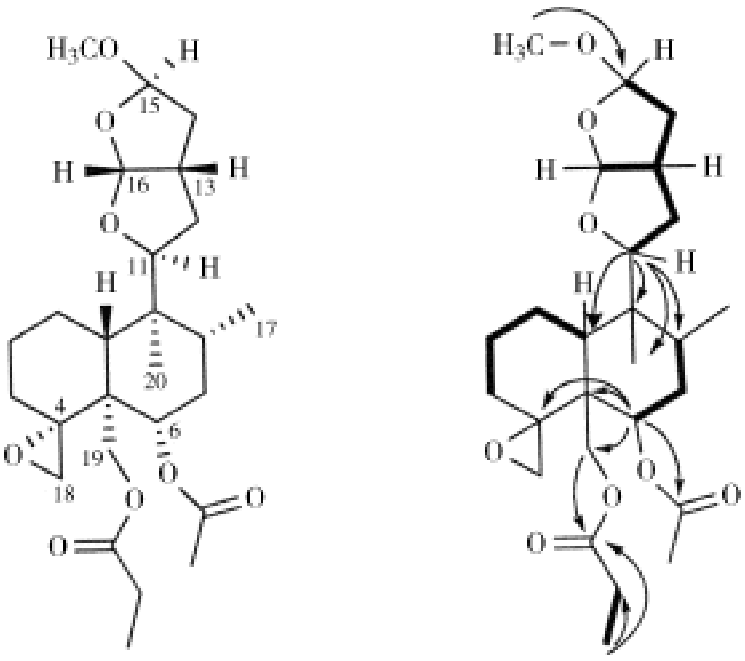
12.0, Hb-19), δ_C 62.0 (t, C-19)], one methine [4.66 (dd, J = 11.4, 4.6, H-6), δ_C 71.9 (d, C-6)] and three substitutions, including an acetoxyl [δ_H 1.92 (s, 3H), δ_C 170.1 (s), 21.2 (q)], a propanoyloxyl [δ_H 2.37 (dq, 7.6, 1.6, 2H), 1.15 (t, 7.6, 3H), δ_C 174.2 (s), 29.6 (t), 9.1 (q)] and one methoxyl group [δ_H 3.30 (s, 3H), δ_C 54.6 (q)]. The HMBC cross-peaks of H-6 C-1′, H_2-19 C-1″, H-3″C-2″, C-1″established the acetoxyl group at C-6 and the propanoyloxyl group at C-19. Meanwhile, the correlations of δ_H 3.30 C-15 established the methoxyl group at C-15. Detailed 2D NMR analysis (Fig.1) further established the planar structure of Scutellin A. The relative configuration of Scutellin A was deduced by its ROESY data. The ROESY correlations of H-11 H_3-20, H_3-17, H-15 and H_3-20 H_2-19 indicated they are on the same side of the decalin and β-orientation. H-6, H-10, $H_β$-18 indicated they are on the other side of the decalin and β-orientation. Thus, Scutellin A was determined to be 15β-methoxy-6α-acetoxy-19-propanoyloxy-4α, 18; 11, 16; 15, 16-triepoxy-neoclerodan.



Scutellin A (**1**)

Fig. 1 COSY (—) and selected HMBC (→) correlations of Scutellin A

Experimental

General Experimental Procedures Optical rotations were measured on a JASCO DIP-370 digital polarimeter. A Tenor 27 spectrophotometer was used for scanning IR spectroscopy. NMR spectra were recorded on Bruker AM-400 and DRX-500 spectrometers with TMS as internal standard. ESIMS was recorded on a finnigan MAT 90 instrument, HRESIMS spectra on VG Auto Spec-3000 spectrometer. Column chromatography was performed on silica gel (200-300 mesh; Qingdao Marine Chemical Inc., Qingdao, People's Republic of China), Sephadex LH-20 (40-70 μm, Amersham Pharmacia Biotech AB, Uppsala, Sweden), and Lichroprep RP-18 gel (40-63 μm, Merck Darmstadt, Germany).

Plant Material The dried aerial part of *Scutellaria barbata* (20 kg) collected in Guangxi Province of China was bought in Kunming Juhua medicinal material market in September, 2007 and a voucher specimen (HH2007092801) is deposited at the State Key Laboratory of Phytochemistry and Plant Resoures in West China, Kunming Institute of Botony, Chinese Academic of Science.

Extraction and isolation Dried and powered aerial part of *S. barbata* (20 kg) was extracted three times with 95% MeOH at 50℃. After evaporating the solvents, the residue was dissolved in H_2O and extracted successively with petroleum ether, EtOAc, and *n*-BuOH, respectively. The EtOAc extract (220 g) was chromatographed over silica gel (200-300 mesh) and eluted with petroleum ether-EtOAc (9∶1, 7∶3, 1∶1, 0∶1) to give four fractions (A-D). Fraction A (54 g) was purified by column chromatography over MCI gel by using 90% MeOH H_2O and MeOH as the eluents. The fraction eluted by 90% MeOH was further purified by Sephadex LH-20 (eluted with MeOH) and silica gel (eluted with petroleum ether Me_2CO 9∶1) to give Scutellin A (54 mg).

Scutellin A (1): $C_{26}H_{40}O_8$, white solide; $[\alpha]_D^{28}$ = -32.7 (c = 0.15, $CHCl_3$); Positive ESIMS m z 503 $[M+Na]^+$; HRESIMS m z 503.2622 $[M+Na]^+$ (calcd 503.2620). IR ν_{max}^{KBr} cm^{-1}: 3432, 1724, 1636, 1628, 1464, 1372, 1255, 1020, 983, 863; ^1H and ^{13}C NMR data, see Table 1.

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表 1　化合物 Scutelin A (1) 的氢谱和碳谱数据

Table 1　The NMR data for Scutelin A (1) in $CDCl_3$

No.	δ_C	δ_H	No.	δ_C	δ_H
1	22.1 t	2.13 (m); 1.57 (m)	14	38.0 t	2.17 (m); 1.65 (m)
2	24.9 t	1.86 (m); 1.38 (m)	15	104.8 d	5.08 (d, 4.8)
3	32.7 t	0.99 brd; 2.08 (m)	16	107.2 d	5.69 (d, 5.4)
4	65.0 s	—	17	16.4 q	0.84 (d, 6.4, 3H)
5	45.5 s	—	18	48.3 t	2.97 (dd, 3.6, 2.4); 2.18 (d, 3.6)
6	71.9 d	4.66 (dd, 11.4, 4.6)	19	62.0 t	4.39 (d, 12.0); 4.83 (d, 12.0)
7	33.3 t	1.44 (m); 1.64 (m)	20	13.9 q	0.94 (s, 3H)
8	36.1 d	1.44 (m)	$6\text{-O-}\underline{CO}CH_3$	170.1 s	—
9	40.0 s	—	$6\text{-O-}CO\underline{CH_3}$	21.2 q	1.92 (s, 3H)
10	48.5 d	1.59 (m)	$19\text{-O-}\underline{CO}CH_2CH_3$	174.2 s	—
11	83.5 d	3.99 (dd, 12.0, 4.0)	$19\text{-O-}CO\underline{CH_2}CH_3$	29.6 t	2.37 (dq, 7.6, 1.6, 2H)
12	32.1 t	1.71 (m); 1.48 (m)	$19\text{-O-}COCH_2\underline{CH_3}$	9.1 q	1.15 (t, 7.6, 3H)
13	39.9 d	2.98 (m)	$15\text{-}OCH_3$	54.6 q	3.30 (s, 3H)

a: ^1H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively

b: Coupling constants were presented in Hertz, unless otherwise indicated, all proton signals integrate to 1H

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《云南植物研究》是国家科委（79）国科发条字 341 号文批准创办的植物学专业学报，是中国科学院主管的全国性自然科学期刊。现为我国植物科学研究发表论文的主要学术性刊物之一，并被评为“中国自然科学核心期刊”，“中国生物学类科技核心期刊”。本刊荣获中科院优秀期刊二等奖（1996）及一等奖（2000）、第二届全国优秀期刊三等奖（1997）及云南省优秀科技期刊一等奖（1997）等，并作为中国科学院首批向美国 SCI 推荐的刊物之一。并入选国家“双效期刊”。本刊所发表的论文在国内生物、农林、医药、轻工等二次文献刊物都有摘报；国外 CA（美国化学文摘）、BA（美国生物学文摘）等从 1980 年起就连续摘报，还有生物科学的当代进展（CABS）、科学引文索引（SCI）的 CI 部分以及俄罗斯文摘杂志（PЖ）和国际农业科技情报系统（Agris）等摘报。乌利希国际期刊指南（UIPD）从 80 年代就刊载本刊出版事宜。现我刊已同 30 多个国家和地区有发行和交换关系；在国内外同行中有一定的影响。本刊现已加中国学术期刊光盘版、中国学术期刊网及万方数据库资源系统。

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